Laboratoire M.S.M.A.P. SARL

Microanalyse Sciences des Matériaux Anciens et du Patrimoine - Etude des objets d'art

STUDY OF A SWORD WITH GOLD INLAID INSCRIPTION (L.: 57 cm) Assumed provenance and period: Khorasan, Samanid, 9th -10th century AD.



Analysis:

B. DUBOSCQ

Doctor of quaternary geology and prehistory. Microanalysis engineer.

C. DUMORA N. POIRIER Archaeometry engineers

NOTICE

The purpose of this study, performed following established norms of scientific integrity, is to carry out scientific investigations to provide analytical data concerning the manufacturing mode of the studied cultural property, the possible weathering of its constitutive material, either natural or artificial and to characterize the deposits or surface treatments on the object.

The investigations based on optical examination and physicochemical analyses of samplings of the object; follow the methods briefly described in the report, which are long-standing standards and protocols employed by the scientific community.

Comparison of the results obtained with the data actually available in the scientific community allows concluding if the physical evidences of the object are consistent or not with its supposed origin and period of time.

These scientific investigations are carried out not taking into consideration historical research, iconography and stylistics statements about the object. Information about provenance, period or attribution of the cultural property are under the responsibility of the owner or its authorized agent and written in the report only as indication. However, this given information is used in the discussion for final statement.

OBJECTIVES

Study of a sword with gold inlaid inscription (L.: 57 cm) Assumed provenance and period: Khorasan, Samanid, 9-10th century AD.

Characterisation of the material from which the object is made, manufacturing technique, weathering, and any surface deposits, for determining if the manufacturing technique as well as the alteration of the object are compatible with its assumed age.

A carbon 14 dating has been performed on the rust from the sword. It gave a calibrated age of 767 AD to 894 AD (92.7% probability) for the death of the wood responsible for the carbon presents in the steel.

SYSTEMS USED

Stereoscopic microscope; inverted optical microscope, Scanning Electron Microscope (SEM) with backscattered electron (BSE) and secondary electron (SE) imaging, coupled with energy-dispersive X-ray element analysis (EDX).

X-Ray radiography was performed by Bureau Veritas working for EADS Astrium in Le Haillan (33, France).

SAMPLES

The study was carried out on different micro samples:

- P1: fragment of the blade obtained by sawing;
- C1 and C2: corrosion products coming from P1;
- P2: gold-coloured inlay fragment, from the inscription;
- P3: silver-coloured globule, from the inscription;

P4: gold coating on the hilt and corrosion products from the surface of the hilt.

Samples P1, C1 and C2 were embedded in resin and a microsection perpendicular to their surface vas performed. Samples P2, P3 and P4 were directly analyzed.

The microsection and the samples were carbon coated for the SEM examination. This operation is partly responsible for the traces of carbon (C) observed on the elementary X-ray spectra.

RESULTS

The analysis of the metal of the blade and the hilt, gold inlaying and coating techniques, state of corrosion of the sword, reveal the following:

• The sword consists of a blade with a short and broad tang, and a separate grip.

The blade

The blade is made out of low carbon steel as evidenced from the ferrite-pearlite microstructure. Silicon
is detected alloyed to the iron, and manganese. This last element is also observed as elongated
copper-enriched manganese sulphide inclusions parallel to the flat of the blade. These elongated
inclusions and the fine-grained homogeneous equiaxed ferrite-pearlite structure are indicative of a final
annealing process of the steel after a probable hammering decarburization of a high carbon steel
(crucible steel?).

The presence of manganese sulphide inclusions could be considered as problematic referring to the modern use of this metal in steel desulfurization processes, but the use of manganese (*magnesia nigra*) to prepare crucible steel is recommended in Arabic written documents from the 11th century (3).

The presence of alloyed silicon is possible in crucible steel (4).

• The gold-coloured inlaid inscriptions were obtained by cutting away the surface of the steel with a chisel, leaving a recess into which a ternary alloy of about 64% silver, 27% copper and 9% gold was molten.

After some trimming of the surface of the blade to scrap-off the metal in excess from the recesses, a depletion gilding of the white coloured alloy has been performed to obtain a gilded inscription. The enriched porous surface was then burnished and probably annealed.

X-Ray radiographs show very acute outlines of the inlays under the steel corrosion products.

If the inlaying techniques in the Islamic world consist usually in hammering ribbons or wires of precious metal on the surface or in grooves in the metal, the technique used in this sword can be compared to some Chinese inlay technique observed for example in *wu tong* objects where thin strands of silverrich low temperature melting alloy are placed in the grooves and melt down or a silver-rich low temperature melting alloy is poured on the wu tong metal surface (5). In this case, the silver-rich alloy has a *liquidus* temperature between 900° and 950°C.

These inlaid inscription are totally encased in the steel corrosion products which is evidence that the inscription is original and cannot have been melted on iron corrosion products (iron hydroxides, iron chlorides), which will be destroyed between 350° to 670°C. Furthermore, evidence of long-term intergranular corrosion of the inlaid metal, matching the corrosion of the steel substrate, is observed.

The hilt

• The metal of the hilt has not been directly sampled, but the corrosion products on the hilt surface indicate the use of a copper-based alloy very probably a leaded brass with some tin. X-Ray radiographs show a heavily corroded metal with a braid-like pattern. Some superficial cracks and the radiographs suggest the use of separate parts in the quillons area. A copper alloy metallic casing seems to tighten these different parts.

The hilt construction is typical of Islamic swords (1). The blade has a short and broad tang inserted in the hilt. A hole in the tang observed on X-Ray radiographs could be indicative of a riveted fixation.

The hilt with the two protruding animal-headed quillons of the cross-guard is covered by a gold foil (gold alloyed with silver, copper and tin).

Corrosion

 Corrosion develops into the blade metal, partly in presence of chlorine. Corrosion processes form iron and iron-silicon corrosion products from the steel. The process is complex and two points can be emphasized:

- In the pitting corrosion areas of the metal, a specific corrosion process concerns the manganese sulphide inclusions, which alter completely to copper iron sulphide inclusions. This phenomenon is observed in steel corrosion (6). Some inclusions also contains mercury whose origin is not explained at our level of analysis.

- In the outer rust layers, secondary metallic copper crystallizations are observed in porosities or cracks of the corrosion layers. If redeposited copper is observed in corrosion processes of steel with low copper content, it usually occurs in contact with the uncorroded metal.

In the case of this object, the copper, sometimes observed with calcium carbonate crystallizations in crack filling is obviously of external origin and indicative of a long-term corrosion in a humid environment. Here, the copper could originate from the corrosion of the hilt - or from a now disappeared scabbard or from abundant copper in the burying environment (proximity with a corroded copper alloy object).

The observation of important exchange of the corroding sword with its alteration environment - calcium presence in the corroded manganese sulphide inclusions from the steel, calcium carbonate and metallic copper filling of voids and cracks in the corrosion layers - are evidence of a natural long-term corrosion process.

These characteristics are compatible with the object's assumed origin and age.

No deposits that could come from a burying environment were observed on the object, but it is certainly the result of the thorough rust cleaning off the blade, to display the inlaid inscription.



Figure 1. Overall views of the sword and samples localization.

1. PRELIMINARY OBSERVATIONS AND SWORD STRUCTURE

The sword, currently in a highly corroded state, consists of a blade with a short and broad tang, visible on the X-ray radiographs (see Fig. 6), inserted in a separate hilt.

The blade is completely covered by layered dark-brown to reddish-brown corrosion products (Fig. 2a) and does not show areas of sound uncorroded metal. It is a grooved blade, with a fuller on each face of the blade. The gold inlaid inscriptions on the blade are partially hidden by these corrosion products (Fig. 2b).

a



same area as b-) The square locates Fig. 2b.

Observations of the degraded inscription show sharp recesses in the blade corrosion products, where the inlays were inserted (Fig. 2b, arrow).

X-Ray radiographs emphasize the very acute outlines of the inlays, under the metal corrosion products (Fig. 2c).

The inlays apparently consist of a foil (Fig. 3a) originally inserted in chiseled recesses on the blade surface, but in some places the inlay appears rather as a thick and massive material than as a foil, with a silvery hue (Fig. 3b, arrow).







Figure 3: Detail views of the inlaid inscription (stereoscopic microscope, a- x14, b- x31).

The different sections of the hilt - the grip, the cross-guard with two animal-headed quillons and the pommel were originally covered with a gold foil.



stripes is perceptible on the front of the grip (Fig. 4a, arrows). This could be the result of a differential wear of the gilding, on a raised pattern. The back is apparently completely gilded (Fig. 4b).



The cross-guard shows cracks (Fig. 5a, arrows) suggesting the association of different metallic parts to build the hilt. This peculiar structure is well observed on the X-Ray radiographs (Fig. 5b).



Figure 5: General views of the cross-guard (a- photograph, b- X-Ray radiograph).

The metal of the hilt shows numerous porosities (Fig. 5b, blue arrows), suggesting à high state of corrosion under a copper alloy metallic casing (Fig. 5b, orange arrows) that tightens the different elements of the hilt up to the pommel.

X-Ray radiographs of the hilt (Fig. 6) show a heavily corroded metal, with an oriented or braid-like (?) structure (Fig. 6c, arrows).



Figure 6: X-Ray radiographs of the hilt (**a**- general view, **b**- detail of the tang of the blade inside the grip, **c**- detail of the grip braid-like structure)

The blade has a short and broad tang (Fig. 6a and b), which is inserted in the grip.

A hole in the tang observed on the X-Ray radiographs (Fig. 6b, arrow) could be indicative of a riveted fixation observed on early Islamic swords (1).

The hilt-blade relation is typical of Islamic swords for which "*The hilt construction ...differs from that of western weapons. The pommel for example, is not a weight to counterbalance the blade but merely a cap terminal for the grip. The tang of the blade is comparatively short and broad, and sometimes set at a slight angle to blade; the grip is either glued to the tang or riveted to it...*

This simple but effective hilt construction was certainly in use by the ninth century." (1).

2. STUDY OF THE METAL OF THE BLADE, THE INLAID INSCRIPTION AND THE HILT

The blade

The metal was sampled at the base of the blade, near the cross-guard (Fig. 7a, arrow). Sawing shows a white metal, under the layered corrosion products.



Figure 8: Detail views of the corrosion products samples (a- C1 and b- C2, stereoscopic microscope, x42)

The blade is made out of low carbon steel as evidenced from the ferrite-pearlite microstructure (Fig. 9a and Fig. 10b).



Figure 9: Detail view (a- inverted metallographic microscope, x500) and global EDX analysis spectrum (b-) of the blade metal.

Silicon is detected (about 1.6%) alloyed to the iron (Fig. 9b), and manganese (about 0.7%). This last element is also observed as elongated manganese sulphide inclusion with copper traces (Fig. 10a) parallel to the flat of the blade (Fig. 10b, arrows).



Figure 10: EDX analysis spectrum of the elongated manganese sulphide inclusions (**a**-) and detail views (SEM, BSE, **b**- x800, **c**- x2000) of the blade metal and corrosion.

The elongated manganese sulphide inclusions and the fine-grained homogeneous equiaxed ferritepearlite structure are indicative of a final annealing process of the steel after a probable hammering decarburization of a high carbon steel (crucible steel?).

The corrosion (Fig. 10b and c, **FeC**) develops in complex multilayered products which will be studied later in this report. A "ghost" microstructure of the steel - mainly pearlite- is visible throughout the corrosion layers (Fig. 10c, blue arrows).

The white flaky material observed on sample P1 and sample C1 consists of aluminum powder, probably part of a restauration process.



The presence of manganese sulphide inclusions could be considered as problematic referring to the modern use of this metal in steel desulfurization processes, but the use of manganese (magnesia nigra) to prepare crucible steel is recommended in Arabic written documents from the 11th century (3).

The presence of alloyed silicon is possible in crucible steel (4).

The inlaid inscription

The inlaid inscriptions have an overall golden colour, but as previously observed (see Fig. 3a), some exhibit a silver-coloured material (Fig. 11, blue arrows) under a golden layer or foil (Fig. 11, orange arrows) that slightly detach from the surface.



Figure 12: Localization (a- stereoscopic microscope, x30) and detail view (b-, SEM, BSE, x100) of Sample P2 of gold coloured inlay.

The metal (Fig. 13b) comprises of a ternary alloy of silver (Ag), gold (Au) and copper (Cu). Low Iron (Fe) and chlorine (CI) are also detected, and traces of nickel (Ni).



Figure 13: Detail view of the gold foil (a- SEM, BSE, x5500) and EDX analysis spectra of the metal (b-) and the products in contact with the metal (c-). Sample P2.

High magnification observation of the gold foil (Fig. 13a) reveals an alveolar or spongy structure, which cavities are partly filled with an iron-rich material (Fig. 13a, orange arrows and 13c).

The spongy structure of the gold foil is indicative of an acidic attack of the silver-gold and copper alloy, very probably to obtain a gold enrichment (depletion gilding).

The iron-rich products, as well as the zinc, nickel, silicon and chlorine detected (Fig. 14c) come from corrosion products of the blade (and the hilt as we will see later).







The gold foil can have a more massive aspect, with a visible granular structure and some hollowing at the grain boundaries (Fig. 14, arrows), which is observed also on the other fragment (Fig. 13a, blue arrows).

This granular structure suggests a final annealing of the inlaid metal.

Figure 14: Detail of the gold foil (SEM, BSE, x4000).

These grain boundaries hollowing-out correspond to an intergranular depletion of the less stable elements from the alloy (copper, silver). This phenomenon is rather indicative of a natural long-term degradation of the gold foil.

Iron oxides and chlorides massively develop as steel corrosion products (Fig. 15a, **FeC**) and partly cover the gold foil (Fig. 15a, **GF**) as previously observed (see Fig. 12).



Figure 15: Detail view (\mathbf{a} -, SEM, BSE, x1000) of the corrosion products in contact with the gold foil and EDX analysis spectra of the iron corrosion products (\mathbf{b} -) and silver corrosion products (\mathbf{c} -). Sample P2.

Silver chlorides (Fig. 15a, arrows, and Fig. 15c) are present inside the steel corrosion products.

These various corrosion phenomena (grain boundary depletion in the gold foil, iron oxide and chloride, silver chloride crystallization) are well developed and seem to occur simultaneously.





The silver-coloured material

A massive sample of the silver-coloured material visible in places under the gold foil was taken from the inlaid inscription (Fig. 16a, arrow).



Figure 16: Localization (**a**-, stereoscopic microscope, x 26) of Sample P3 on the blade and global EDX analysis spectrum of the alloy (**b**-).

The material consists of a ternary alloy of 64% silver, 27% copper and 9% gold. It has a two-phase dendritic structure.

FeC

Figure 17: Detail views of sample P3 microsection (**a**-, metallographic microscope, x500, **b**- SEM, BSE, x6000) and EDX analysis spectrum of the gold-enriched phase inside the copper-depleted areas. Sample P3.

The metal surface shows a preferential corrosion of the copper-rich phase, inducing the depletion of copper (Cu) leaving a gold-enriched phase (Fig. 17b, orange arrows) inside the depletion-induced porosities.

Steel corrosion products from the blade (Fig. 17a and b, **FeC**) are in direct contact with the alloy and partly fill the porosities.

The surface of the alloy shows a microporous structure

(Fig. 17a and b, blue arrows) similar to that of the gold foil previously examined.

We propose therefore the following process for the gold inlaying:

The gold inlaid inscriptions were obtained by cutting away the surface of the steel with a chisel, leaving a recess into which a ternary alloy of about 64% silver, 27% copper and 9% gold was molten. After some trimming of the surface of the blade to scrap-off the metal in excess from the recesses, a depletion gilding of the silver-coloured alloy has been performed to obtain a gilded inscription. The enriched porous surface was then burnished and probably annealed.

If the inlaying techniques in the Islamic world consist usually in hammering ribbons or wires of precious metal on the surface or in grooves in the metal, the technique used in this sword can be compared to some Chinese inlay techniques observed for example in wu tong objects, where thin strands of silver-rich low temperature melting alloy are placed in the grooves, or a silver-rich low temperature melting alloy is poured on the wu tong metal surface, or a (5). In this case, the silver-rich alloy has a liquidus temperature between 900° and 950°C.

These inlaid inscriptions are totally encased in the steel corrosion products which is evidence that the inscription is original and cannot have been melted on iron corrosion products (iron hydroxides, iron chlorides), which will be destroyed between 350° to 670°C. Furthermore, evidence of long-term intergranular corrosion of the inlaid metal, matching the corrosion of the steel substrate, is observed.

The silvery aspect of part of the inlays very probably comes from wear of the gold-enriched surface.





The two-phase metal comprises of a white silver-rich (Fig. 17b, Ag) and a pink copper-rich phase (Cu). Both phases contain gold. Some iron and nickel-rich inclusions are observed inside the alloy.

The Hilt

The metal

The metal of the hilt has not been directly sampled, but the corrosion products from the hilt surface observed in sample P4 (Fig. 18a, C and Fig. 18b). Iron (Fe), zinc (Zn), copper (Cu) and tin (Sn) are detected indicating the use of a copper-based alloy very probably a leaded brass with some tin (?).



Figure 18: View of sample P4 (a-, SEM, BSE, x200) and EDX analysis spectrum of the corrosion products (b-).

As zinc, lead and tin are not detected - at this level- in the blade corrosion products, they are characteristic of material constituting the hilt.

Magnesium, aluminum and silicon can originate from sedimentary material from the burying environment incorporated in the corrosion products.

The gold foil

Analysis of a fragment of the gold foil on the hilt (Fig. 19a) detects a gold (Au) -copper (Cu) - silver (Ag) and tin (Sn) alloy (Fig. 19b).



Figure 19: View of sample P4 (a-, SEM, BSE, x5000) and EDX analysis spectrum of the metal (b-).

Traces of iron (Fe) and zinc (Zn) are present, which could come respectively from the blade and from the hilt corrosion products.

b

Another fragment of gold foil was analyzed. The gold seems to have a different composition, with gold (Au) mainly alloyed to copper (Cu) and only trace of silver (Ag) and no tin. This suggests several phases of gilding.



Figure 20: View of sample P4 (a-, SEM, BSE, x1500) and EDX analysis spectrum of the corrosion products (b-).

2. THE CORROSION PROCESSES

The corrosion processes have been studied on microsections of massive samples (P1, C1 and C2).

Corrosion (Fig. 21a, C) develops into the blade metal (Fig. 21a, M) and forms iron and iron-silicon oxide and hydroxides layered corrosion products from the steel (Fig. 21b and c).

cps/el





Figure 21: View of sample P1 (**a**-, SEM, BSE, x400) and EDX analysis spectra (**b**- and **c**-) of the corrosion products.

The silicon level is variable and can be high (Fig. 21c).

Traces of manganese are detected, as well as sulphur, chlorine, sodium and potassium.

Chlorine is also massively detected in some corrosion products (Fig. 22b).



Figure 22: Detail view (**a**-, SEM, BSE, x3000) of the blade corrosion and EDX analysis spectrum of the steel corrosion products (**b**-) and of the elongated inclusion (**c**-). Sample C1.

This corrosion process is complex and several points can be emphasized:

In the corroded metal, where the ghost steel microstructure is still visible (Fig. 22a, blue arrows), elongated inclusions are observed (Fig. 22a, orange arrows). They correspond to elongated copperenriched manganese sulphide inclusions present in the steel (see Fig. 11).

In the corroded area, there is a compositional change

of the inclusions, for which iron and sulphur are still detected (Fig. 22c), but manganese is very low and copper is present (compare with the spectrum in Fig. 11a). Some mercury (Hg) is also detected.

In the outer part of the corroded metal, where the ghost microstructure has completely disappeared, the inclusions are still present (Fig. 23a, orange arrows), with the same compositional change, which corresponds to a leaching of the manganese (Fig. 23b) and a significant copper enrichment.



Figure 23: Detail view (a-, SEM, BSE, x1000) and EDX analysis spectrum of the corroded manganese sulphide inclusions. Sample C2.



This phenomenon, corresponding to the alteration of the manganese sulphide inclusions to copper sulphide inclusions, is observed in steel corrosion (6).

The detection of calcium in some of the inclusions (Fig. 23b) is indicative of an exchange with the environment of the object, as some cracks or porosities, close to these inclusions contain crystallized calcium carbonate (Fig. 23a, **Ca**) that may only occurs from the outside of the object.

The mercury observed in some inclusions (cf. Fig. 22c) could also originate from the object environment.

In the outer rust layers, secondary metallic copper crystallizations (Fig. 24a and b, Cu and arrows and Fig. 24c) are observed in porosities, cracks of the corrosion layers, or voids between steel corrosion products crystallizations.



Figure 24: Detail views (SEM, BSE, **a-** x1000, **b-** x2000) and EDX analysis spectrum (**c-**) of the metallic copper recrystallization in the steel corrosion products.

If redeposited copper is observed in corrosion processes of steel with low copper content, it usually occurs in contact with the metal.

In the case of this object, the copper, sometimes observed with calcium carbonate (Fig. 24a and b, **Ca**) crystallizations in cracks filling is obviously of external origin and indicative of a long-term corrosion in a humid environment.



Here, the copper could originate from the corrosion of the hilt - or from a now disappeared scabbard or from abundant copper in the burying environment (proximity with a corroded copper alloy object).

These characteristics, and in particular the evidence of important exchange of the corroding object with its alteration environment - calcium presence in the corroded manganese sulphide inclusions from the steel, calcium carbonate and metallic copper filling of voids and cracks in the corrosion layers - are evidence of a natural long-term corrosion process.

No deposits that could come from a burying environment were observed on the object, but it is the result of the thorough rust cleaning off the blade, to display the inlaid inscription.

Bibliography

1 - M. Fahri Furat, 1998 - A brief Study on swords, *Şarkiyat Mecmuası*, n°8, p. 319-330.

2 - D.A. Scott, 1991 - Metallography and microstructure of Ancient and historic Metal. The Getty Conservation Institute, p. 16.

3 - J. Le Coze, 2013 - Mines d'acier, magnesia nigra - le manganese dans les aciers, depuis quand? *Matériaux et Techniques*, 101, 404, p.1-18.

4 - S. Sirinivasan, 2007 - On higher carbon and crucible steels in southern India: further insights from Mel-Siruvalur, Kodumanal and Pattinam. *Indian journal of History of Science*, 42, 4, p. 673-695.

5 - M. Wayman, P. Craddock, 1993 - Wu Tong, a neglected Chinese decorative technology. *Metal plating and Patination,* S; La Niece and P. Craddock edit., p. 128-134.

6 - A.R. Daud, 1996 - Corrosion of Sulphide Inclusions in Stainless Steel. *Pertanika Journal of Science and Technology*, 4 (2), p. 201-207.